



AFRL-AFOSR-VA-TR-2016-0244

Ultrafast Spectroscopy of Proton-Coupled Electron Transfer (PCET) in Photocatalysis

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07/08/2016
Final Report

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REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 11-06-2016		2. REPORT TYPE Final Report			3. DATES COVERED (From - To) March 14, 2013 - March 14, 2016	
4. TITLE AND SUBTITLE Ultrafast Spectroscopy of Proton-Coupled Electron Transfer (PCET) in Photocatalysis				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER FA9550-13-1-0128		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Dawlaty, Jahan M.				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Southern California Department of Contracts and Grants 3720 S. Flower St. Cub 301 Los Angeles CA 90089-0701 (phone: 213-740-6058)					8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research Program Officer: Dr. Michael Berman 875 N. Randolph St. Suite 325, Rm 3112 Phone: (703) 696-7781 Arlington, VA 22203					10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
					11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION A: Distribution approved for public release.						
13. SUPPLEMENTARY NOTES						
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15. SUBJECT TERMS Proton transfer, Proton-coupled electron transfer, excited state proton transfer, photocatalysis, ultrafast dynamics, proton conductivity.						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jahan Dawlaty	
U	U	U	SAR	11	19b. TELEPHONE NUMBER (Include area code) 607-351-0731	

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Ultrafast Spectroscopy of Proton-Coupled Electron Transfer (PCET) in Photocatalysis

Jahan Dawlaty, University of Southern California

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Abstract

The main goal of this project is to understand the mechanisms of proton-coupled electron transfer reactions, with particular emphasis on their relevance and utility for solar-to-fuel light harvesting. The main focus of our work has been identifying coupling between the electronic and protonic degrees of freedom in a wide range of materials. In particular, we have sought to identify **themes and principles that dictate how protons move in the aftermath of an electronic excitation**. The results can be divided into three groups. First, we have studied a molecule with excited state proton transfer capability and two identical protons for transfer. We have correlated the electronic charge density redistribution to proton transfer and have identified that electronic relaxation after a single proton transfer extinguishes the propensity of the second proton to transfer. Our work on this system led us to the interesting concept of photobasicity, where light excitation of a photobase can be used to remove a proton from a target molecule. This phenomenon has the potential to be used in photocatalysis. Our next finding was identifying how electronic charge transfer couples to hydrogen bonding and proton transfer in a hydrogen bonded solid. This is based on an experiment that connects excitations on three different energy scales (electronic, OH vibrations, and low-frequency lattice motion) to each other all at once. Extensive pump-probe and Raman spectroscopy experiments reveal that upon electron transfer, low frequency lattice modes are excited which in turn modulate the hydrogen bonding and inter-site proton transfer. Our third area of work is more zoomed out of the molecular scale and aims to connect light excitation to bulk protonic conductivity. In this work we have relied upon the analogy between a semiconductor and an electrolyte to induce proton conductivity in a photoacid doped electrolyte. This work is a step towards bringing electronic and protonic devices to the same platform. Finally, we have had a long-standing effort for understanding the influence of pH on fundamental electrochemical reactions. This work has resulted in to unique insights into the intricacies of the pH dependence of electrochemical rates. In summary, the results of our work lays a foundation engineering systems, both molecular and materials scale, that take advantage of coupling between electronic and protonic degrees of freedom to drive chemistry.

1. Ultrafast resolution of an intramolecular acid/base reaction in the electronically excited state:

Excited State Intramolecular Proton Transfer (ESIPT) is the conceptual stepping stone for understanding coupled electron-proton motion in photocatalysis. The questions of interest are: How soon after an electronic excitation the proton moves? What type of charge rearrangements are required to induce protonic motion? In a molecule with two transferrable protons, do both protons transfer, or does one impede the transfer of the other?

Towards this end, we have studied coupled electron-proton motion in the excited state of a recently synthesized dye. As shown in figure (1), we have resolved the emergence of the proton transfer band and have identified that the proton transfer process takes in the order of 300 fs or faster. We have also identified that although two transferrable protons exist, only one of them is transferred in the excited state. This finding is relevant for designing multi-proton redox agents, where transfer of several protons in the excited state is desirable.

An important finding in our work was the difference in proton transfer time between the doubly protonated molecule (diol) and a modified singly protonated version of it in which the proton was substituted with a methoxy group (ethoxyl). We found out that proton transfer time in ethoxyl was significantly faster than in diol. With calculations from the group of Tom Miller at Caltech, we arrived at the conclusion that in the diol a balance of hydrogen bonding between the two sides of the molecule results into slightly larger hydrogen bond lengths compared to the ethoxyl. Such a hydrogen bond balance idea seems to explain the observed kinetics.

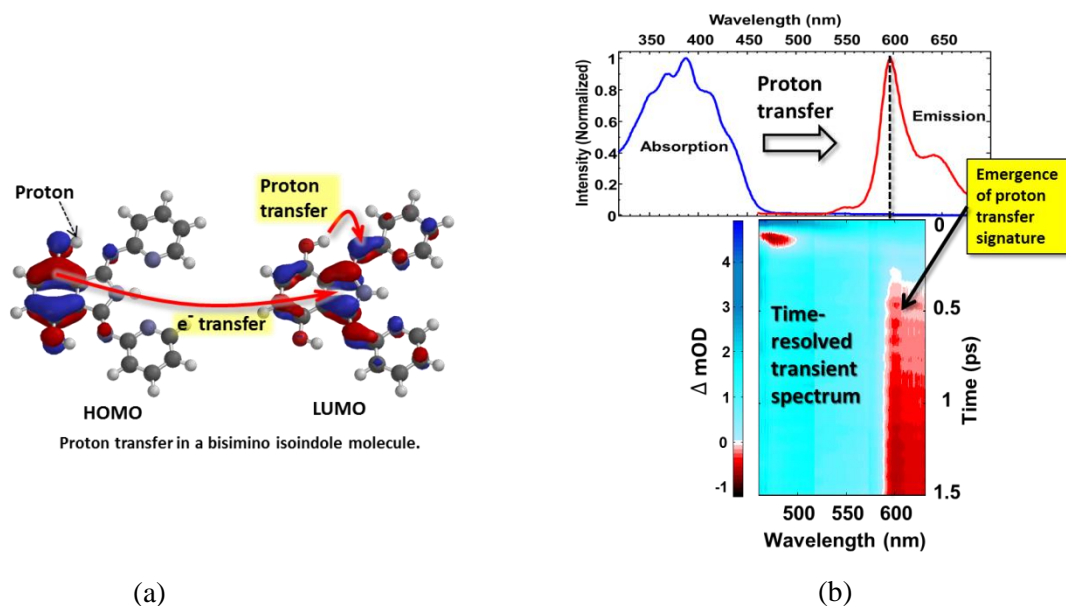


Figure 1. (a) Electron proton transfer in optically excited bisimino isoindole model molecule. (b) The proton is transferred in less than 300 fs in the excited state, as evidenced by the emergence of stimulated emission at the proton transfer band.

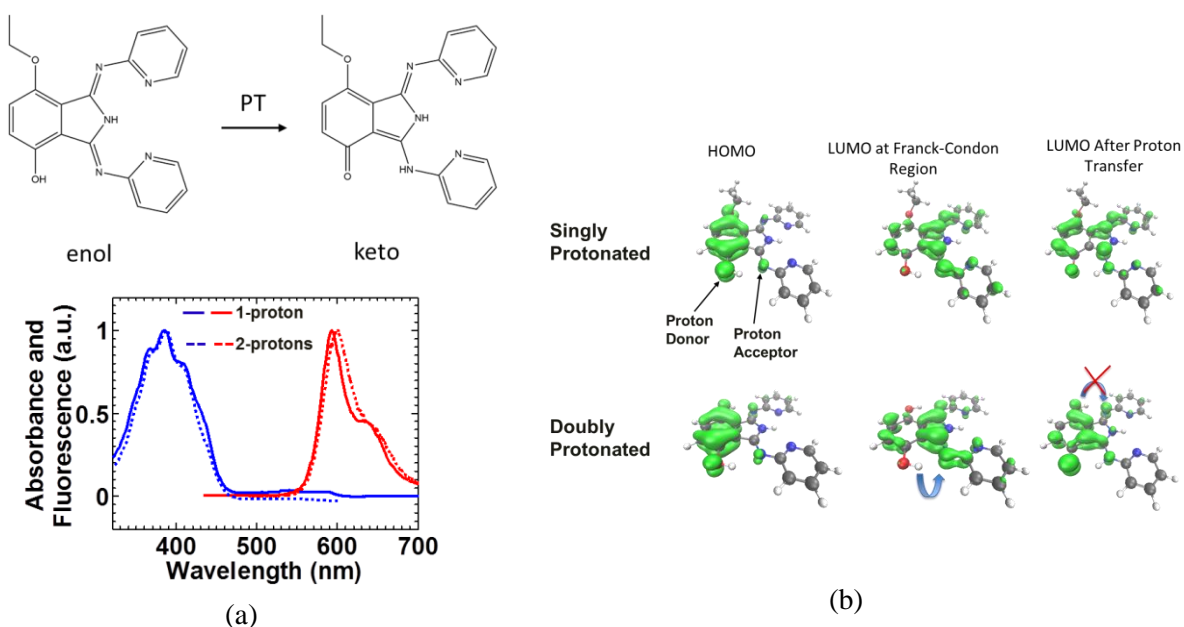


Figure 2. (a) Similarities in the absorption and emission spectra between the singly protonated molecule (ethoxy-ol) and the doubly protonated (diol) molecule suggests that only a single proton transfers occurs in the excited state in both cases. (b) Computational work explains the origin of one proton transfer in the excited state. After the first proton transfer, electronic charge density (green) re-flows back towards the proton donor side of the molecule. This charge reflow extinguishes the drive for the second proton transfer.

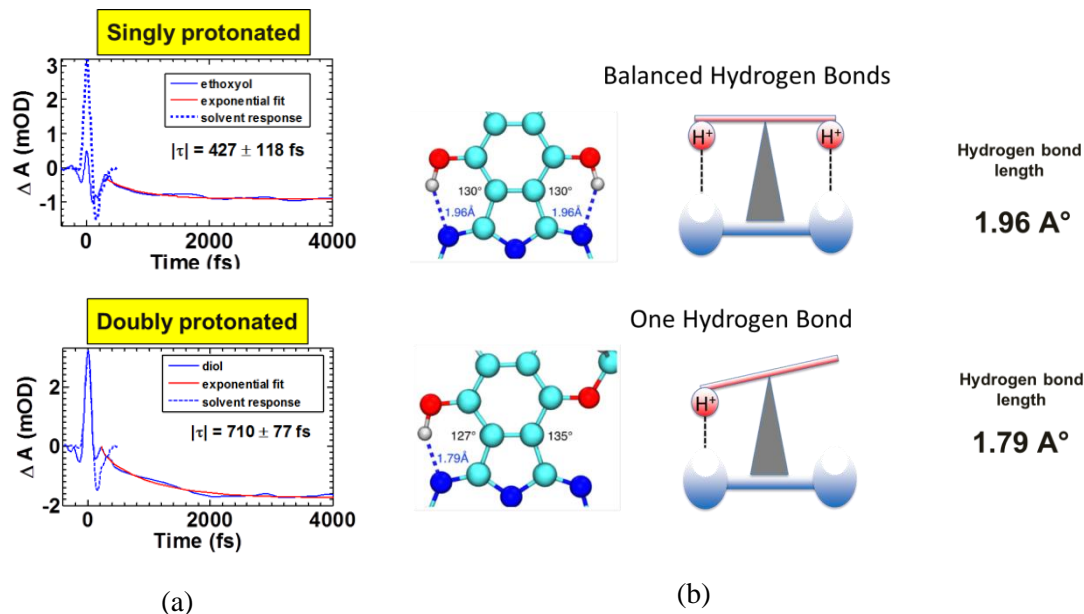


Figure 3. (a) The ethoxyol (top) exhibits faster proton transfer time compared to diol (bottom). (b) Computational work by Miller group at Caltech revealed the origin of this difference. The molecule acts like a seesaw. When both sides are hydrogen bonded, the average bond length is longer than when one side is hydrogen bonded. This difference in hydrogen bond length is consistent with the experiment and alludes to a partially tunneling mechanism in the excited state proton transfer. Further kinetic isotope tests confirmed this mechanism.

An important outcome of this work was the observation of excess charge density on the proton acceptor in our calculations. Such excess charge density seems to be part of the drive for proton transfer. In simple terms, as the oxygen atom becomes more acidic, the nitrogen atom becomes more basic in the excited state. We hypothesized that such excess charge density can be optically generated in an isolated molecule without the proton donor residing on the same molecule. Thus a drive for proton removal or photobasicity can be induced in a molecule optically.

To test this hypothesis we measured ground and excited state basicity in a series of 5-substituted quinolines using the conventional Förster cycle. Indeed, as expected quinoline exhibited photobasicity, and furthermore its photobasicity showed a linear trend with respect to the electron-withdrawing capability of the substituent. Thus we not only demonstrated photobasicity in this molecule, but also showed how to control and tune it. Such molecules, when incorporated in oxidation catalysts, can serve as proton removal agents.

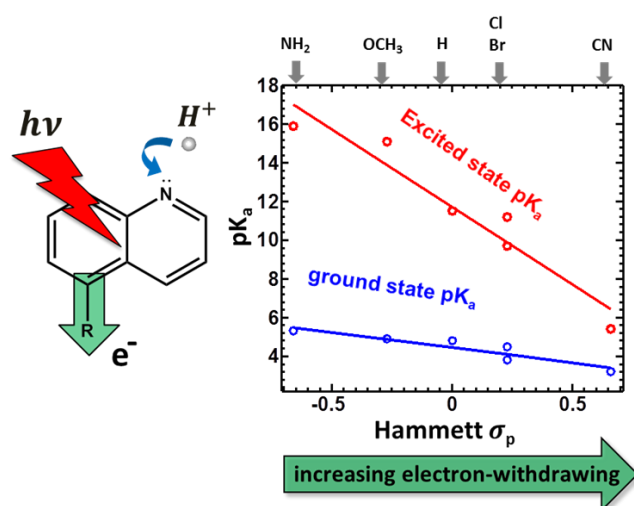


Figure 4. The concept of photobasicity was identified and explored as a consequences of our intramolecular proton transfer study. Excitation of a nitrogen containing heteroaromatic results into piling of charge density on the nitrogen, which renders it more basic. This photobasicity can be tuned by the electron-withdrawing strength (related to the Hammett parameter) of the substituent R. Our work reveals that the excited state pK_a is more sensitive to the electron-withdrawing strength of the substituent than the ground state.

2. Electron and proton transfer in a solid made of the canonical redox couple benzoquinone and hydroquinone:

PCET reactions involved in natural and artificial photocatalytic systems involve several electron-proton transfer steps, and are often embedded in a complicated environment with inconvenient spectroscopic access. To study PCET, simple and tractable models are desired. Towards that goal, we have prepared co-crystals of one of the simplest two-electron two-proton redox couple hydroquinone/benzoquinone.

The crystals are ideal charge transfer systems that involve both electron transfer and hydrogen bonding. We have used a short pulse to induce excited state charge transfer from hydroquinone to benzoquinone, and then measured the dynamics that follows the charge transfer using broad-band transient reflection. Our results suggest that the two redox couples come close to each other in the excited state and execute an underdamped vibrational motion lasting for several picoseconds. Evidence from Raman spectroscopy and observation of a Raman band at the frequency of the observed oscillations confirms that the oscillations arise from the relative face-to-face motion of the two redox couples. On an interesting note, albeit less relevant to photocatalysis, we have identified an acoustic shockwave propagating through the crystal. Our measurement was capable of measuring the dispersion of the acoustic shockwave in this crystal.

Finally, we have probed this material in the OH stretch region after pumping it electronically. We observe that the probe in the OH stretch region also shows oscillations. Variation of phase and amplitude of these oscillations as a function of probe frequency reveal that there are transitions in the OH stretch region that are directly modulated by the low frequency phonons in the crystal. This experiment is possibly the clearest example of demonstrating coupling between electronic, low-frequency phonons, and hydrogen bonding degrees of freedom in a chemical system.

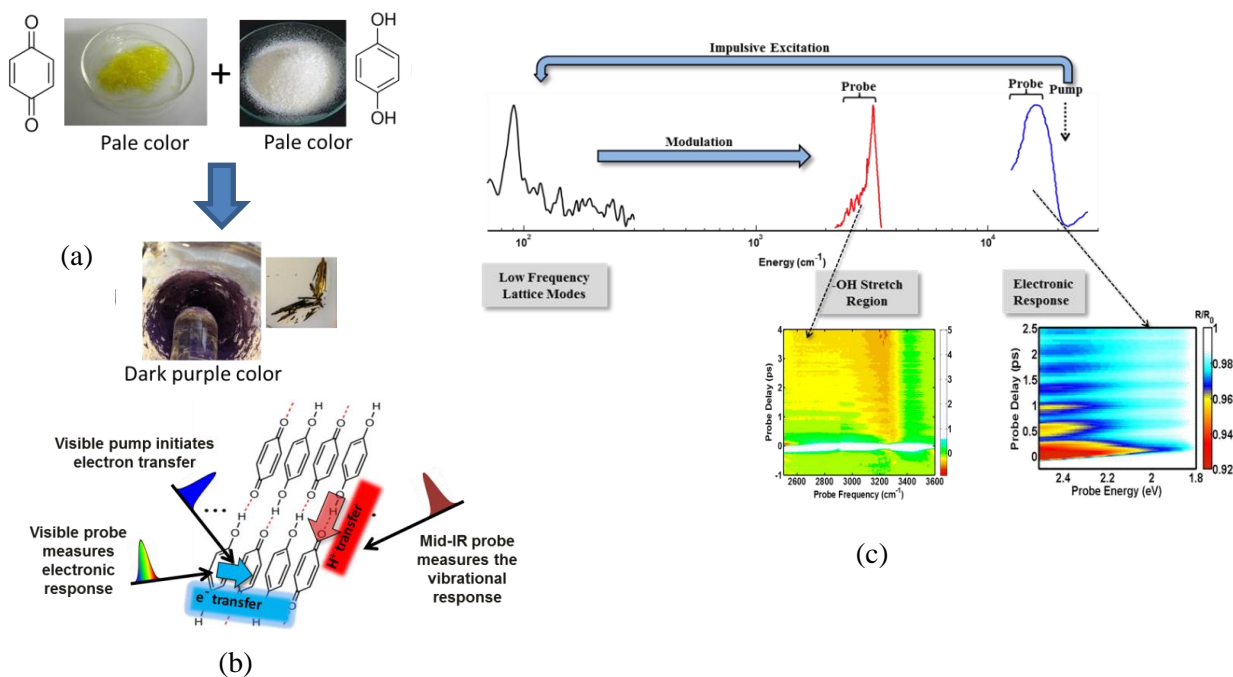


Figure 5. (a) Formation of the charge-transfer hydrogen-bonded crystal quinhydrone. (b) Schematic of the optically induced charge transfer and the ensuing protonic motion initiated and probed by visible and mid-IR pulses respectively. (c) The response of quinhydrone over a large range of energy (notice the logarithmic scale). Our experiments identify the interplay of motions over such a large range of energy.

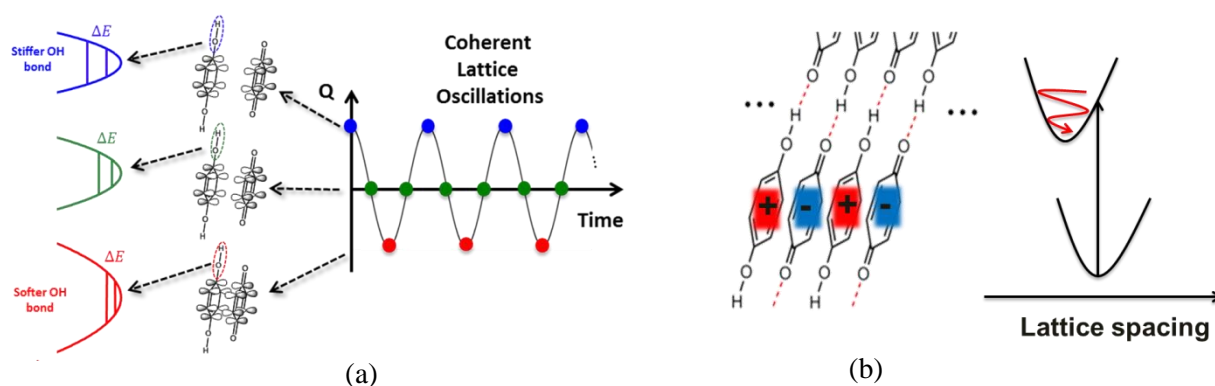


Figure 6. (a) Mechanism of coupling between low frequency lattice modes and OH stretch. Lattice excitations modulates the distance between the charge transfer pairs. At small distances, HQ and BQ have better electronic overlap, thus charge density on HQ is reduced. This leads to a weaker OH bond. The reverse of this happens at larger separations. (b) Mechanism of coupling between electron transfer and low frequency lattice vibrations. Optical excitation leads to rapid charge transfer from HQ to BQ. The ensuing slower lattice adjustment to this charge transfer results into launching low frequency optical phonons which modulate the HQ-BQ distance shown in (a).

3. Bulk Proton Conductivity Influenced by Electronic Excitation.

To couple electronic excitation to bulk protonic conductivity, we have exploited an analogy between semiconductors and electrolytes. The bandgap of a semiconductor is the barrier towards generation of mobile charge. The same scenario can be envisaged for water, in which the water dissociation equilibrium can be related to a free energy or a gap towards ion pair generation. To access this gap optically, it is necessary to introduce photoacids into water, which release protons upon light excitation in the visible range. Thus in direct analogy to photoconductivity in a semiconductor, one arrives at a proton photoconductivity effect. We have exploited this analogy to perform the first report of photoinduced proton conductivity.

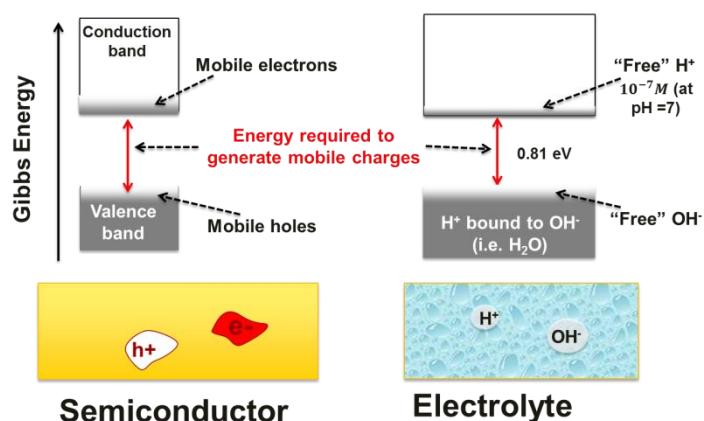


Figure 7. The analogy between a conventional semiconductor and an electrolyte or ionic liquid such as water.

We have used a common photoacid, hydroxypyrene trisulfonic acid (HPTS), as our optical handle for modulating ionic conductivity. The photoacid is dissolved either in water or in a polymer matrix between two electrodes. The AC conductivity of the material is measured in dark and in light. The experiments clearly show that shining light changes the AC impedance of the material. The formalism that connects impedance to ionic concentration already exists in the literature. Using the conventional models for ionic conductivity, we can show that increase in ionic conductivity due to light plausibly explains the observed impedance change.

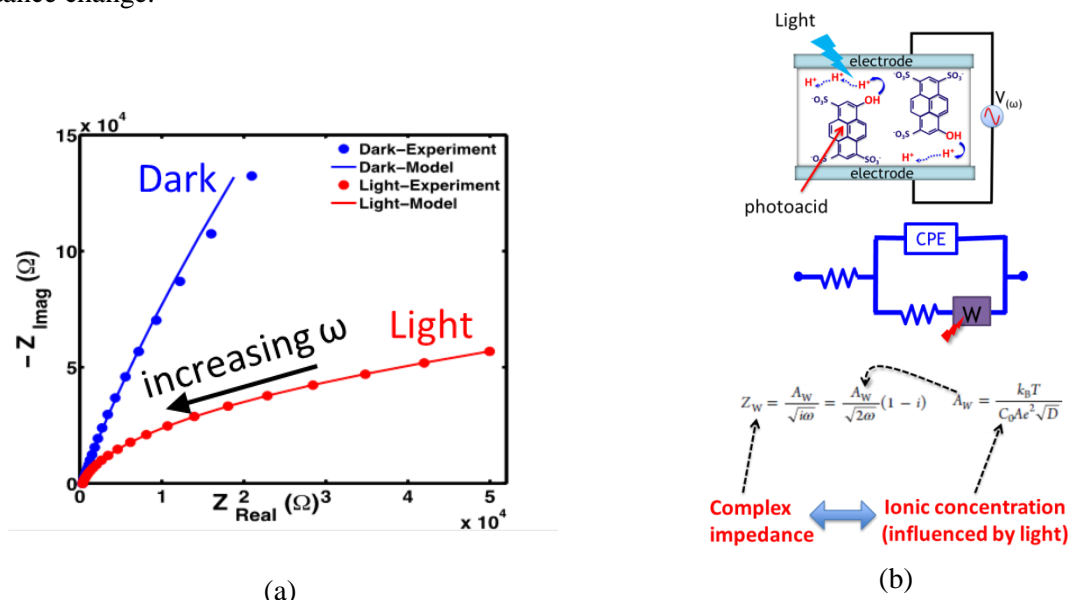


Figure 8. (a) Complex impedance of a photoacid doped material measured in the presence and absence of light. (b) A conventional circuit model with light-sensitive ionic impedance is used to explain the observed impedance spectra.

4. Global View of the Influence of Protons on Water Oxidation Kinetics and the Introduction of Continuous Electrochemical Kinetic Diagrams.

The coupling between electron and proton kinetics is not restricted to the ultrafast realm. Change in pH is known to influence both the rate and the onset potential of the water oxidation reaction. In this work, we did an extensive study of the influence of pH on electrochemical water oxidation on hematite.

For the first time, we prepared diagrams that show the electron transfer parameter and the proton reaction order in two-dimensional plots. These diagrams provide a birds-eye view of the kinetic influence of protons on electrochemical reaction rate. Important information such as the acidic and basic mechanisms, surface adsorption and saturation, and mass-transport limits, can be gleaned from such diagrams in a relatively simple and visual way.

The measured parameters, particularly the differences between the electron transfer parameter in the acidic and basic limits is interpreted in light of a model that accounts for concerted deprotonation and electron transfer from surface adsorbed water or hydroxyl groups.

We have extended these diagrams for hydrogen evolution as well. Currently, we are working on understanding the origin of the variation of rate and its sensitivity to pH and potential.

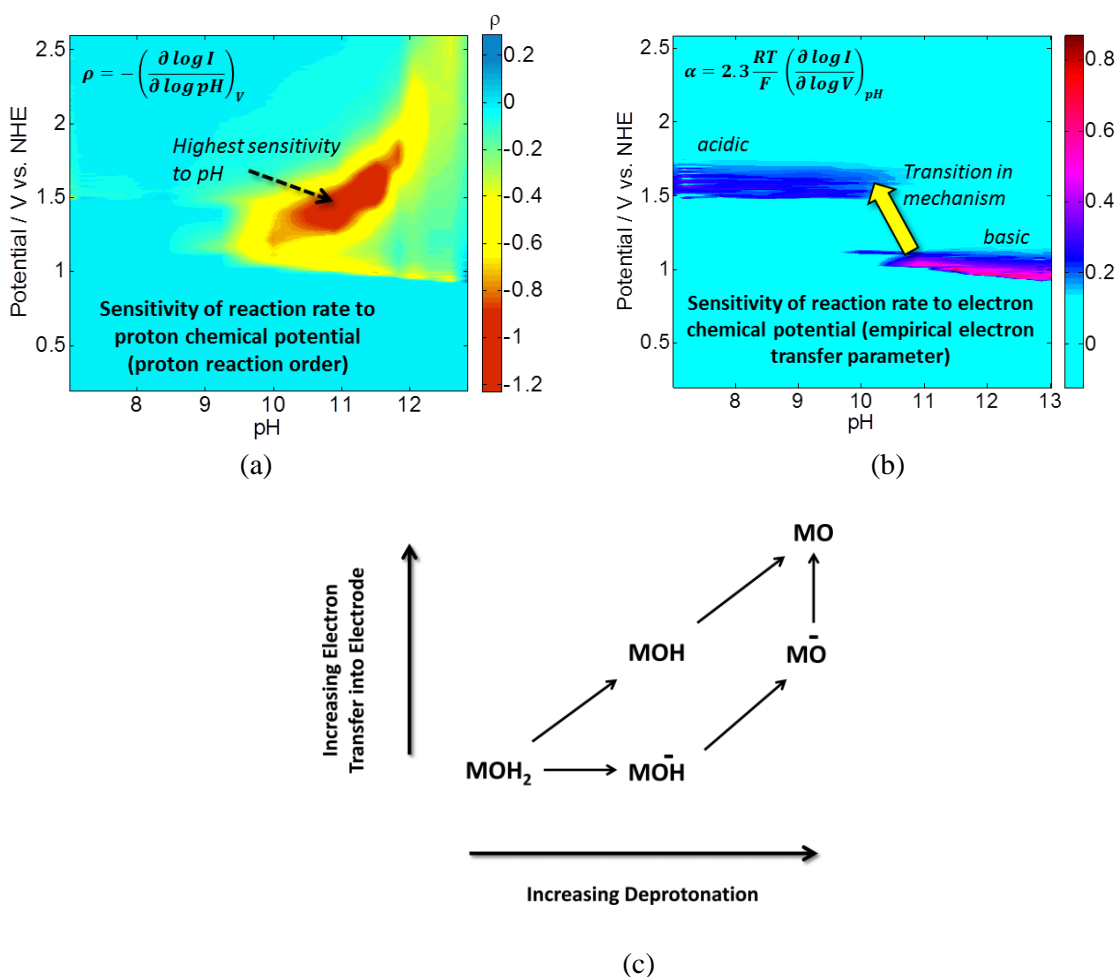


Figure 6. (a-b) The proton reaction order and electron transfer parameter measured for water oxidation on hematite. Such two-dimensional representations were prepared for the first time in our group. (c) The observations in the diagrams are explained on the basis of a model that involves surface protonation and electron transfer. All diagonal arrows are hypothesized coupled electron-proton transfer (CPET) steps.

Impact

The findings of this work are anticipated to impact several aspects the basics of our knowledge proton dynamics, in particular in the context of proton requiring redox reactions. The three most immediately applicable consequences of work are listed below.

- **Use of photobasicity in catalysts:** We propose that a photobase be incorporated as a functional component of a conventional organometallic catalyst and tuned to transduce light excitation to proton removal power. This will be the first time that the proton removal barrier of a redox reaction is tackled separately with assistance from light.
- **Establishing a new paradigm for proton transfer and balance of hydrogen bonds:** Our work on the “seesaw” model for hydrogen bonding reveals that even in the excited state, proton transfer is sensitive to minute changes in distance. We anticipate that the seesaw mechanism studied in this work can be exploited in catalyst design with the aim of modulating hydrogen bonding. For example, one can foresee design themes in which the strength of hydrogen bonding in the core of a catalyst is finely modulated (and perhaps photochemically actuated) by a counterbalanced hydrogen bond located farther away. To realize such goals, it is necessary to study this effect further. In particular, if the fulcrum of the seesaw is composed of a single C-C bond and hydrogen bonds are placed along the body of the seesaw at variable distances, a potential extension of the mechanical “law of the lever” to molecular scales may be achievable.
- **Proton conductivity controlled by light:** Our work on proton conductivity initiated by light opens the possibility of driving protonic currents towards a heterogeneous catalytic surface that consumes protons. For that reason, further work is needed to control unidirectional flow of protons (i.e. photocurrent), as opposed to merely increasing photoconductivity.

Publications Supported by This Grant:

1. Ultrafast Carrier Dynamics in Hematite Films: The Role of Photoexcited Electrons in the Transient Optical Response, S. Sorenson, E. Driscoll, S. Haghighat, J. Dawlaty, J. Phys. Chem. C, 118 (41), 23621 (2014)
2. Continuous Representation of the Proton and Electron Kinetic Parameters in the pH-Potential Space for Water Oxidation on Hematite, S. Haghighat, J. Dawlaty, J. Phys. Chem. C, 119 (12), 6619 (2015)
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4. Electronic State-Resolved Electron-Phonon Coupling in an Organic Charge Transfer Material from Broadband Quantum Beat Spectroscopy, A. Rury, S. Sorenson, E. Driscoll, J. Dawlaty, J. Phys. Chem. Lett. 6, 3560 (2015)
5. Controlling Proton Conductivity with Light: A Scheme based on Photoacid Doping of Materials, S. Haghighat, S. Ostresh, J. Dawlaty, J. Phys. Chem. B, 120, 1002 (2016)
6. Intermolecular electron transfer from intramolecular excitation and coherent acoustic phonon generation in a hydrogen-bonded charge-transfer solid, A. Rury, S. Sorenson, J. Dawlaty, J. Chem. Phys., 144, 104701, (2016)
7. Photobasicity in Quinolines: Origin and Tunability via the Substituents' Hammett Parameters, E. Driscoll, J. R. Hunt, J. Dawlaty, J. Phys. Chem. Lett., 7, 2093 (2016)
8. A Molecular Seesaw: How Increased Hydrogen Bonding Hinders Excited State Proton Transfer, R. Welsch, E. Driscoll, J. Dawlaty, T. Miller III, (submitted)
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Ultrafast Spectroscopy of Proton-Coupled Electron Transfer (PCET) in Photocatalysis

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FA9550-13-1-0128

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

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Please describe and include any notable dates

Do you plan to pursue a claim for personal or organizational intellectual property?

Changes in research objectives (if any):

Change in AFOSR Program Manager, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

Jun 11, 2016 13:35:45 Success: Email Sent to: dawlaty@usc.edu